Table VII. Oxidation of Isobutene at Different Pressures

Pressure, cm	$[H_t]$, M	$[OAc_t]$, M	[Tl(III)], M	k'_{exptl}, M^{-1} sec^{-1}	k'_{calcd}, M^{-1} sec^{-1}	$\frac{[Tl(OAc)_2^+]}{[Tl(III)]}$
401	1.01	1.140	0.0019	0.83	0.83	7.8×10^{-5}
212	1.01	1.140	0.0019	0.89	0.83	7.8×10^{-5}

of reaction mixtures except the thallic ion. For ethylene and propylene this side reaction was insignificant. Determination of olefin solubilities has been described.[11] The order in olefin was determined only for isobutene since the reaction in strong acid solution had previously been demonstrated to be first order in olefin.[1,9] A constant volume reactor[11] was used for these measurements. The rate was measured by change in pressure. Since the concentration of Tl(III) was small (*ca.* 10^{-3} M), the change in pressure was small compared to the total pressure, so the pressure was assumed to be constant and the data were plotted as a first-order reaction. The second-order rate constant was then calculated from the solubility at that pressure. Data on the two runs at lower pressures are given in Table VII.

Measurement of Equilibrium Constants. The pH of the solutions was measured with a Beckman pH meter. Readings tended to drift with time, probably because of diffusion of chloride ion from the saturated calomel electrode into the solution. Thus, the first reading on a freshly prepared solution was taken as the correct pH reading.

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Electron Donor–Acceptor Interactions of Molecular Iodine with Olefins

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Abstract: A study of the interactions of olefins and related hydrocarbons with molecular iodine has been made using a gas–solid chromatographic technique. Relative equilibrium constants for olefin–iodine complexes have been determined and are compared with the corresponding equilibrium constants for silver nitrate–olefin complexes. A pronounced inverse secondary deuterium istope effect on complex formation has been observed.

Molecular iodine interacts with molecules containing π-electron systems to form weakly bonded association products which can be described as electron donor–acceptor complexes.[4,5] Such complexes are characterized by strong absorption bands in the ultraviolet, commonly called "charge-transfer bands." According to the theory of Mulliken and co-workers,[6–8] the charge-transfer absorption maximum, $\lambda_{\max}$, is a function of the vertical ionization potential of the donor, I_D^V, the vertical electron affinity of the acceptor, E_A^V (1.7 ev for iodine),[9] and the interaction and resonance energy differences between ground and dative states of the complex. The binding energies of molecular compounds are small relative to $I_D^V - E_A^V$, and therefore $\lambda_{\max}$ itself does not provide a suitable measure of complex stability. So far, the extinction coefficients or integrated intensities have not been accurately measured and correlated with the thermodynamic equilibrium constant for complex formation.

Complexing equilibrium constants were first obtained from spectrophotometric data by Benesi and Hildebrand[10] from measurements of extinction coefficients for solutions of varying donor and acceptor concentrations in an "inert" solvent. Haymann[11] has recently discussed the reliability of spectrophotometric methods in comparison with the partition method. Neither method has been broadly applied to complexes of iodine with the simpler olefins.

Equilibrium constants have been determined for Ag^+–olefin complexes in ethylene glycol solution using gas chromatographic methods.[12–14] Solid 1,3,5-trinitrobenzene–olefin complexes have also been investigated chromatographically,[15] and, although equilib-

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rium constants could not be calculated from the data, relative stabilities of the molecular compounds were derived. The application of gas–solid chromatography to the study of iodine–olefin complexes is the subject of the present paper.

Experimental Section

Columns containing iodine (Baker Analyzed reagent grade) on three different support materials were prepared in the following manner.

Firebrick. (1) Johns-Manville Chromosorb P (38.8 g, 30–60 mesh) was mixed with a solution of 9.65 g of iodine in 200 ml of diethyl ether. The ether solvent was slowly evaporated from the continually agitated slurry under reduced pressure, and a 16-ft length of 4-mm i.d. Pyrex glass tubing was filled with the resulting iodine–firebrick mixture.

(2) Chromosorb P (42.2 g, 42–60 mesh) was mixed with a solution of 10.0 g of iodine in 250 ml of diethyl ether, and the solvent was evaporated as before. A 20-ft length of 0.125-in. o.d. Type 304 stainless steel tubing was washed with amyl acetate, carbon tetrachloride, and acetone, dried, and filled under pressure with the packing mixture.

Silanized Celite. F and M Scientific Diatoport S (20.4 g, 60–80 mesh) was mixed with a solution of 5.0 g of iodine in 150 ml of diethyl ether, and the solvent was evaporated as before. A 20-ft length of cleaned stainless steel tubing, 0.125-in. o.d., was filled under pressure with this packing.

Silanized Firebrick. F and M Scientific Chromosorb P, AW, DMCS (20.2 g, 60–80 mesh) (Johns-Manville Chromosorb P, acid washed, and treated with dimethyldichlorosilane) was mixed with a solution of 5.0 g of iodine in 150 ml of diethyl ether, and the solvent was evaporated as before. A 20-ft length of cleaned stainless steel tubing, 0.125-in. o.d., was filled under pressure with this packing.

All packings were uniformly colored, dry, and flowed easily. The columns were flushed overnight at 0° with dry helium to remove remaining traces of volatile material. They were thermostated in an ice–water slush at 0° during operation to reduce bleeding of the iodine substrate to an experimentally acceptable level and to increase retention times. Samples of 10^{-3} to 10^{-1} μmole were flushed onto the columns from a U-shaped bypass injector (volume $\sim$2 cc), using helium as the carrier gas. A 10:1 stream splitter system, inserted between the injection system and the column, reduced the effective injection time to a few tenths of a second. Detection was with a flame ionization detector. The recorder chart speed was generally 1 in. min^{-1}, except for very late peaks when slower speeds were used.

Most hydrocarbons were Phillips Petroleum Co., pure or research grades. Deuterated olefins were obtained from Merck Sharp and Dohme, Montreal, Canada.

Adjusted retention times (t_r') of the eluents were obtained by subtracting the retention time (t_r) of methane from the retention times of the hydrocarbons. The interaction of methane with the iodine and the support was assumed to be negligible. Relative retention times ($r_{1,2}$) were determined using 2,3-dimethylbutane as standard. All retention data were obtained from at least duplicate experiments. Methane samples were run once an hour to assure a constant flow rate; 2,3-dimethylbutane was likewise run approximately hourly in order to allow for minor fluctuations in column condition and operating conditions. This routine was adhered to for experiments with all but the first column prepared with firebrick support which was used for preliminary data, some of which were not redetermined.

To calculate linear flow rates, retention times for methane injected with a syringe into the carrier gas stream about 8 in. upstream of the refrigerated column were measured. The flow rate thus determined is an average taken over the entire column length. The deviation from this average is greatest at high flow rates where the pressure drop across the column is most severe. Average flow rates used were between 0.92 and 5.7 cm sec^{-1}.

Results

Experimental Data. The adjusted retention times relative to 2,3-dimethylbutane, $r_{1,2}$, are given in Table I for the paraffins and in Table II for the unsaturated hydrocarbons investigated. With column I (iodine on Chromosorb P, AW, DMCS) measurements were made at three average flow rates, U, of 0.92, 1.93, and 4.43 cm sec^{-1}. With columns II (iodine on Diatoport S), and III and IV (iodine on untreated firebrick), the average flow rates used were 3.4, 5.7, and 4 cm sec^{-1}, respectively. The values of the height equivalent to a theoretical plate, H, listed in Tables I and II only for column I at U = 1.93 cm sec^{-1}, have been determined from the equation

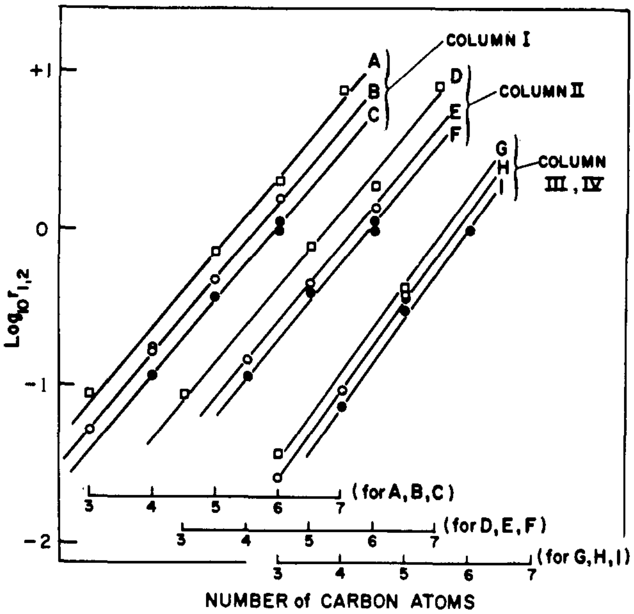

Figure 1. Plot of the logarithm of the relative retention times ($r_{1,2}$) of paraffins and cycloparaffins against the number of carbon atoms (A, D, G: cycloparaffins; B, E, H: *n*-paraffins; C, F, I: branched paraffins).

$$H\,(\text{cm}) = L\,(\text{cm}) \Big/ 16\left[\frac{t_r\,(\text{min})}{\text{peak width (min)}}\right]^2$$

where L denotes the column length and t_r the unadjusted retention time. For column V (uncoated support, Chromosorb P, AW, DMCS) $r_{1,2}$ values are also listed, determined at flow rates of 1.5 and 2.2 cm sec^{-1}.

Paraffins show a more or less regular chromatographic behavior on these columns, as evidenced by relatively sharp symmetrical peaks (small values of H in Table I) and constant relative adjusted retention times, $r_{1,2}$, independent of the carrier gas flow rate. The $r_{1,2}$ values obtained with column II are very similar to those obtained at the three flow rates on column I; small differences observed with some of the paraffins are explainable by the inaccuracies due to very small retentions on column II. On the other hand, the $r_{1,2}$ values on columns III and IV (with untreated firebrick as the support) do differ somewhat from those on column I. These differences are well shown in the plots of log $r_{1,2}$ against the number of carbon atoms given in Figure 1; good linear plots are obtained for the retention data on column I, with separate parallel lines for *n*-alkanes, branched alkanes, and cycloparaffins. The corresponding values on column II fall approximately on the same lines but show greater scatter. The data for columns III and

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Table I. Retention Data for Paraffins and Cycloparaffins on Solid Iodine at 0 °[a]

	$r_{1,2}$							H, cm
	I							
Hydrocarbon	U_1	U_2	U_3	II	III	IV	V	I (U_2)
C_3H_8	0.052	0.045	...	...	0.026	...	0.049	0.78
n-C_4H_{10}	0.164	0.174	0.163	0.150	0.092	0.100	0.163	0.66
i-C_4H_{10}	0.116	0.122	0.121	0.113	0.075	...	0.130	0.68
n-C_5H_{12}	0.474	0.504	0.489	0.450	0.360	0.390	0.499	0.78
i-C_5H_{12}	0.370	0.383	0.388	0.400	0.293	0.311	0.403	0.56
n-C_6H_{14}	1.55	1.53	1.50	1.63	...	...	1.54	1.8
2-Me-pentane	1.11	1.13	1.09	1.15	...	...	1.07	0.65
2,3-DiMe-butane	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.55
c-C_3H_6	...	0.087	...	0.088	0.037	...	...	1.0
c-C_5H_{10}	0.718	0.738	0.717	0.775	0.360	0.400	0.721	1.4
c-C_6H_{12}	2.00	2.03	1.97	1.88	...	...	1.87	1.3
c-C_7H_{14}	...	7.69	7.62	8.00	...	...	...	4.4

[a] Column I: I_2 on Chromosorb P, AW, DMCS; flow rates $U_1 = 0.92$, $U_2 = 1.93$, $U_3 = 4.43$ cm sec^{-1}; II: I_2 on Diatoport S; III, IV: I_2 on Chromosorb P; V: uncoated support, Chromosorb P, AW, DMCS. The $r_{1,2}$ values represent t_r'/t_r' (2,3-dimethylbutane), where the average t_r' (2,3-dimethylbutane) is 14.9 (I, U_1), 7.05 (I, U_2), 3.07 (I, U_3), 0.80 (II), 8.9 (III), and 9.0 min (IV).

Table II. Retention Data for Unsaturated Hydrocarbons on Solid Iodine at 0 °[a]

	$r_{1,2}$							H, cm
	I							
Hydrocarbon	U_1	U_2	U_3	II	III	IV	V	I (U_2)
$RCH{=}CH_2$								
Ethylene	0.00	0.00	...	0.00	0.004	0.005	0.012	...
Propylene	0.33	0.46	0.06	0.08	1.0	0.75	0.058	27.6
Propylene-*d*$_6$	0.57	0.72	0.06	0.20	2.20	...	...	50.7
Butene-1	1.75	2.35	0.91	2.04	10.2	3.7, 2.8	0.17	21.7
Pentene-1	5.54	4.57	3.40	4.68	...	10.0	0.47	16.0
3-Me-butene-1	1.65	2.17	1.17	2.11	...	5.4	0.33	14.5
$R_2C{=}CH_2$								
Isobutene	0.23	0.24	0.22	0.18	0.45	0.22	0.19	0.76
2-Me-butene-1	0.78	0.79	0.75	0.80	...	1.01	0.52	1.08
2-Me-pentene-1	1.89	1.94	1.92	1.92	...	...	1.38	1.27
cis-$RCH{=}CHR$								
cis-Butene-2	0.58	0.65	0.56	0.65	2.32	0.75	0.24	2.45
cis-Butene-2-*d*$_8$	0.71	0.81	0.68	1.07	3.57	1.20	...	2.76
cis-Pentene-2	2.12	2.13	1.87	2.22	10.1	3.1	0.64	3.80
trans-$RCH{=}CHR$								
trans-Butene-2	0.27	0.28	0.28	0.30	0.44	0.22	0.20	1.08
trans-Butene-2-*d*$_8$	0.29	0.29	0.29	0.35	0.60	0.26	...	1.13
trans-Pentene-2	0.80	0.79	0.75	0.81	1.63	0.85	0.60	1.32
$R_2C{=}CHR$								
2-Me-butene-2	0.81	0.81	0.78	0.74	1.23	0.72	0.68	0.98
2-Me-pentene-2	2.03	2.08	2.09	1.98	...	...	1.81	1.05
$R_2C{=}CR_2$								
$(CH_3)_2C{=}C(CH_3)_2$	2.43	2.52	2.58	2.47	...	2.48	2.15	1.60
Cycloolefins								
Cyclopentene	1.64	1.67	1.51	1.77	...	1.45	0.80	5.63
Cyclohexene	...	19.1	20.3	40	...	24	2.8	9.21
Cycloheptene	...	10.7	10.6	13.1	...	9.3	7.9	7.24
Diolefins								
Butadiene-1,3	0.65	0.85	0.48	0.81	2.00	0.70	0.20	12.2
Butadiene-1,3-*d*$_6$	0.89	1.27	0.73	1.22	...	1.02	...	19.0
Acetylene derivatives								
Acetylene	...	...	0.05	0.04	0.02	...	...	...
Me-acetylene	0.25	0.26	0.26	0.15	0.23	...	...	1.4
$CH_3C{\equiv}CD$	0.25	0.26	0.26	...	...	...	...	1.4
Aromatic hydrocarbons								
Benzene	4.71	4.49	4.60	4.6	...	...	3.50	7.60
Toluene	...	...	...	12.6	...	...	...	...

[a] Description of the columns I–V and the flow rates, U_1–U_3, are given in the text and in Table I. The $r_{1,2}$ values are relative to 2,3-dimethylbutane taken as unity. The t_r' values for 2,3-dimethylbutane are quoted in footnote *a*, Table I.

IV are less extensive; they seem to be mutually consistent, but the plots of log $r_{1,2}$ against the number of carbon atoms, although again approximately linear, have slightly different slopes from those for columns I and II.

The difference between columns I and II, on one hand, and columns III and IV, on the other, is further accentuated in working with olefins. The untreated firebrick columns (III and IV) showed considerable instability and very poor reproducibility and self-consistency, tending to degenerate rapidly with use. After several days operation, larger sample sizes of olefins were required with these columns to produce a standard signal from the detector, and shortly thereafter certain olefins were irreversibly adsorbed on the column. This behavior is not understood but presumably arises, at least in part, from a direct interaction between the untreated firebrick surface and iodine, resulting in an enhancement of the activity of the iodine surface. On the other hand, reproducibility and self-consistency were good for the columns with silanized firebrick (column I) and silanized Celite (column II); no degradation in column performance was observed during several weeks of constant use. At comparable flow rates, all hydrocarbons were retained about four times longer on columns with silanized firebrick (Chromosorb P, AW, DMCS) than with silanized Celite (Diatoport S). This factor is roughly that of the ratio of the BET surface areas of the two types of support.

In view of the uncertain behavior of the two columns (III and IV) with the untreated firebrick as the support, the data obtained with these columns are not too reliable quantitatively. The data from column II are not subject to the same uncertainty, but some of these data are also of low precision because of the short retention times ($t_r' < \sim 0.5$ min). Thus, from a quantitative point of view, the greatest reliance should be placed on the data from column I, especially at the slowest flow rate used ($U_1 = 0.92$ cm sec^{-1}). Nevertheless, it was felt that at least some of the derived values should be reported for all the four iodine-coated columns, in order to show that in spite of the indicated difficulties the results are on the whole very similar.

The uncoated support (column V, Chromosorb P, AW, DMCS) behaved with the paraffins in a very similar manner as when coated with iodine (column I), especially taking into account the difficulties which exist in making such a comparison. The $r_{1,2}$ values in Table I are the same, and the t_r' and the H values are also comparable. With the olefins, on the other hand, the retention times are always longer on the iodine-coated column, and in most cases the difference is very striking, as shown in Table II. There is a similar difference in the sharpness of the peaks; on column V the H values for olefins (not shown in Table II) are relatively small, while on the iodine-coated columns the olefin peaks tend to be much broader, as shown by the large H values in Table II.

Evaluation of the Equilibrium Constants from the Retention Times. Comparison of the data in Tables I and II shows that the olefins are retained considerably longer on the iodine-coated columns than the corresponding paraffins. In order to obtain a quantitative measure of this specific interaction of olefins with the solid iodine deposit, we have adopted the following approach. In Table II the retention data are grouped together for various structural types of olefins. In each group the relative retention times ($r_{1,2}$) increase with the number of carbon atoms, indicating a superposition of the effect of the size of the molecule, similar to that exhibited by the corresponding paraffins, upon the specific effect of the interaction of the olefinic double bond with the solid deposit. To separate the two effects, it is assumed that the over-all adsorption process can be treated as consisting of the following equilibria

$$\underbrace{A_c' \underset{k_{-c}'}{\overset{k_c'}{\leftrightarrows}} A_s' \underset{k_{-s}'}{\overset{k_s'}{\leftrightarrows}}}_{V_s' \text{ (exposed support)}} \underbrace{A \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}}}_{V_g \text{ (gas phase)}} \underbrace{A_s \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} A_c}_{V_s \text{ (solid iodine)}}$$

where A stands for a hydrocarbon molecule (olefin or paraffin), A_s is a molecule adsorbed on iodine (without being complexed), A_c is a molecule complexed with iodine, A_s' and A_c' are, respectively, the molecules adsorbed and complexed on the exposed "support"; V_g, V_s, and V_s' are the volume elements corresponding to the gas, iodine, and the exposed "support" phases, respectively. The following equilibrium constants are defined: $K_s = [A_s]/[A]$, $K_c = [A_c]/[A_s]$, $K_a = K_sK_c = [A_c]/[A]$, and $K_s' = [A_s']/[A]$, $K_c' = [A_c']/[A_s']$, $K_a' = K_s'K_c' = [A_c']/[A]$.

From the material balance of the molecules transported through the column it follows that

$$V_g\frac{\partial[A]}{\partial t} = V_gD\frac{\partial[A]}{\partial x^2} - V_gU\frac{\partial[A]}{\partial x} - (V_gk_s[A] - V_sk_{-s}[A_s]) - (V_gk_s'[A] - V_s'k_{-s}'[A_s'])$$

$$V_s\frac{\partial[A_s]}{\partial t} = (V_gk_s[A] - V_sk_{-s}[A_s]) - (V_sk_c[A_s] - V_sk_{-c}[A_c])$$

$$V_s\frac{\partial[A_c]}{\partial t} = (V_sk_c[A_s] - V_sk_{-c}[A_c])$$

$$V_s'\frac{\partial[A_s']}{\partial t} = (V_gk_s'[A] - V_s'k_{-s}'[A_s']) - (V_s'k_c'[A_s'] - V_s'k_{-c}'[A_c'])$$

$$V_s'\frac{\partial[A_c']}{\partial t} = (V_s'k_c'[A_s'] - V_s'k_{-c}'[A_c'])$$

D is the gaseous diffusion coefficient of A, and U is the linear velocity of the carrier gas ($L/U = t_0$, the "dead" time). If all the species are mutually in equilibrium, the above equations reduce to

$$q\frac{\partial[A]}{\partial t} = D\frac{\partial^2[A]}{\partial x^2} - U\frac{\partial[A]}{\partial x}$$

where

$$q = 1 + \frac{V_s}{V_g}(K_s + K_a) + \frac{V_s'}{V_g}(K_s' + K_a')$$

The solution is (for a "plane source")

$$[A] = \frac{[A_0]}{2(\pi D/q)^{1/2}t^{1/2}} \exp\left(-\frac{x^2}{4Dt} + \frac{U}{2D}x - \frac{U^2}{4Dq}t\right)$$

Maximization with respect to t at $x = L$ leads to the familiar simple relation

$$q = t_r/t_0 \text{ or } \frac{V_s}{V_g}K_s(1 + K_c) + \frac{V_s'}{V_g}K_s'(1 + K_c') = \frac{t_r'}{t_0} \quad (1)$$

Evidently, the equilibrium constants of interest cannot be calculated directly from the measured adjusted retention times (t_r'), and the following simplifying assumptions become necessary: (1) for an olefin and its structurally analogous paraffin $(K_s)_{ol} = (K_s)_{par}$ and $(K_s')_{ol} = (K_s')_{par}$, and (2) paraffins do not complex with iodine or with the exposed support $[(K_c)_{par} = (K_c')_{par} = 0]$. Under such conditions it is possible to define normalized adjusted retention times, $t_n' = (t_r')_{ol}/(t_r')_{par}$, for the olefins relative to their structurally analogous paraffins. It will at first be assumed also that olefins do not complex with the exposed support so that, in view of eq 1, under such conditions

Table III. Relative Equilibrium Constants of Adsorption (K_a) and Complexing (K_c) of Olefins with Solid Iodine at 0 °[a]

	K_a/K_a^* (eq 3)						K_c/K_c^* (eq 5)					
	I						I					
Hydrocarbon	U_1	U_2	U_3	II	III	IV	U_1	U_2	U_3	II	III	IV
$RCH{=}CH_2$												
Propylene	0.67	0.87	...	...	0.44	...	2.2	3.3	...	...	1.6	...
Propylene-d_6	1.2	1.4	...	...	1.0	...	3.7	5.5	...	...	3.5	...
Butene-1	3.8	4.6	(1.9)	3.8	4.5	5.5	3.8	4.6	(1.9)	3.8	4.5	5.5
Pentene-1	12.1	8.6	(7.4)	8.5	...	14.7	4.2	3.0	(2.5)	2.8	...	3.8
3-Me-butene-1	3.1	3.8	(2.0)	3.4	...	7.8	1.4	1.7	(0.8)	1.3	...	2.5
$R_2C{=}CH_2$												
Isobutene	0.27	0.25	0.26	(0.13)	0.17	...	0.38	0.35	0.34	(0.17)	0.20	...
2-Me-butene-1	0.99	0.87	0.91	0.80	...	1.1	0.44	0.40	0.38	0.30	...	0.34
2-Me-pentene-1	1.9	1.7	2.1	1.6	...	...	0.28	0.26	0.31	0.20	...	...
cis-$RCH{=}CHR$												
cis-Butene-2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
cis-Butene-2-d_8	1.3	1.4	1.3	1.9	1.6	1.7	1.3	1.4	1.3	1.9	1.6	1.7
cis-Pentene-2	4.0	3.4	3.5	3.6	4.4	4.2	1.4	1.2	1.1	1.4	1.1	1.1
trans-$RCH{=}CHR$												
trans-Butene-2	0.26	0.23	0.29	0.30	0.15	0.19	0.26	0.23	0.29	0.30	0.15	0.19
trans-Butene-2-d_8	0.30	0.24	0.31	0.40	0.23	0.24	0.30	0.24	0.31	0.40	0.23	0.24
trans-Pentene-2	0.78	0.62	0.66	0.73	0.57	0.71	0.27	0.21	0.22	0.24	0.15	0.18
$R_2C{=}CHR$												
2-Me-butene-2	1.1	0.90	1.0	0.68	0.42	0.63	0.47	0.41	0.42	0.25	0.13	0.20
2-Me-pentene-2	2.3	2.0	2.5	1.7	...	...	0.33	0.31	0.38	0.21	...	...
$R_2C{=}CR_2$												
$(CH_3)_2C{=}C(CH_3)_2$	3.4	3.2	4.0	3.0	...	2.3	0.56	0.56	0.65	0.44	...	0.23
Cycloolefins												
Cyclopentene	2.2	2.0	2.0	20	...	1.6	0.50	0.47	0.44	0.39	...	0.40
Cyclohexene	...	36	46	(76)	...	...	...	3.1	3.8	(6.1)	...	...
Cycloheptene	...	6.3	7.6	(10.3)	...	...	...	0.14	0.16	(0.19)	...	...
Diolefins												
Butadiene-1,3	1.2	1.4	8.1	1.3	0.85	0.92	1.2	1.4	0.81	1.3	0.85	0.92
Butadiene-1,3-d_6	1.7	2.3	1.4	2.1	...	1.4	1.7	2.3	1.4	2.1	...	1.4
Acetylene derivatives												
$CH_3C{\equiv}CH$	0.46	0.46	...	...	(0.09)	...	1.4	1.8	...	...	(0.3)	...
$CH_3C{\equiv}CD$	0.46	0.46	...	...	...	...	1.4	1.8	...	...	...	...
Aromatics												
Benzene	6.5	5.2	6.7	5.5	...	...	0.53	0.45	0.54	0.44	...	...
Toluene	...	...	...	9.5	...	...	...	...	...	...	...	...

[a] The values are relative to those of *cis*-butene-2 taken as unity. Description of the columns I–IV and the flow rates, U_1–U_3, are given in the text and in footnote *a* of Table I.

$$K_a = \frac{V_g}{V_s}\frac{[(t_r')_{ol} - (t_r')_{par}]}{t_0} \qquad (2)$$

The value of V_s/V_g (and V_s'/V_g') cannot be determined experimentally, and it is therefore only possible to measure the relative values of the equilibrium constants, choosing one olefin as the standard (in the present work *cis*-2-butene is taken as the standard and all the values for the standard are marked with an asterisk). Therefore

$$K_a/K_a^* = [(t_r')_{ol} - (t_r')_{par}]/[(t_r')_{ol} - (t_r')_{par}]^* \qquad (3)$$

Also, since $K_a = K_sK_c$, eq 1 is in this approximation reduced to

$$K_c = \left(1 + \frac{V_s'K_s'}{V_sK_s}\right)(t_n' - 1) \qquad (4)$$

and thus

$$K_c/K_c^* = (t_n' - 1)/(t_n' - 1)^* \qquad (5)$$

Equations 3 and 5 permit calculations of the relative values of K_a and K_c, subject to the validity of the simplifying assumptions made. (The same equations are also valid when the gas phase and the adsorbed molecules are not fully equilibrated, as will be mentioned below.) The values of K_a/K_a^* and K_c/K_c^* calculated from eq 3 and 5 are listed in Table III, with the data again grouped together for the structurally related hydrocarbons. The values obtained at the three flow rates on column I and on columns II, III, and IV are on the whole reasonably mutually consistent, in spite of the already-mentioned quantitative uncertainties and poor reproducibility on columns III and IV and very small retention times on column II. The data obtained on column I, especially at the slowest flow rate used (U_1), are believed to be quantitatively the most reliable. At the highest flow rates on this column the values of the equilibrium constants for the monoalkylethylenes ($RCH{=}CH_2$) tend to be smaller and are considered unreliable. With these olefins the H values are particularly large, and the very broad peaks coupled with much smaller t_r' values make the relative equilibrium constants quite uncertain (these values are in parentheses in Table III and are omitted from the mean values given below).

As already mentioned, eq 3 and 5 are valid only if olefins do not form complexes with the exposed support, *i.e.*, $(K_c')_{ol} = 0$. This is perhaps true in spite of the finding that the uncoated support (column V) retains olefins somewhat longer than their structurally analogous paraffins, because iodine may tend to cover preferentially the active sites of the support responsible for the increased retention of olefins. The other extreme possibility is that olefins interact with the exposed support in the iodine-coated columns in exactly the same manner as they do with the pure support (column

Table IV. Mean Values of the Relative Equilibrium Constants at 0° for Solid Iodine on Column I[a]

Hydrocarbon	K_a/K_a^* I_2 (eq 3)	K_a/K_a^* I_2 (eq 6)	K_c/K_c^* I_2 (eq 5)	K_c/K_c^* I_2 (eq 7)	K_c/K_c^* Ag^{+b}	$(K_c')_{SF}$
$RCH{=}CH_2$						
Propylene	0.8	0.9	2.8	3.2	1.5	0.18
Propylene-d_6	1.3	1.5	4.6	5.5	1.7	...
Butene-1	4.2	5.2	4.2	5.2	1.9	0.03
Pentene-1	10.4	12.7	3.6	4.4	1.4	*c*
3-Me-butene-1	3.5	4.3	1.6	1.9	1.7	*c*
$R_2C{=}CH_2$						
Isobutene	0.26	0.16	0.36	0.23	1.0[d]	0.43
2-Me-butene-1	0.92	0.80	0.41	0.35	0.9	0.30
2-Me-pentene-1	1.9	1.4	0.28	0.21	0.5[d]	0.29
cis-RCH=CHR						
cis-Butene-2	1.0	1.0	1.0	1.0	1.0	0.46
cis-Butene-2-d_8	1.3	1.5	1.3	1.5	1.1	...
cis-Pentene-2	3.6	4.0	1.2	1.4	1.2	0.28
trans-RCH=CHR						
trans-Butene-2	0.26	0.22	0.26	0.22	0.30	0.20
trans-Butene-2-d_8	0.28	0.25	0.28	0.25	0.35	...
trans-Pentene-2	0.69	0.56	0.23	0.19	0.32	0.20
$R_2C{=}CHR$						
2-Me-butene-2	1.0	0.45	0.43	0.20	0.17	0.69
2-Me-pentene-2	2.3	0.58	0.34	0.09	0.12[d]	0.69
$R_2C{=}CR_2$						
$(CH_3)_2C{=}C(CH_3)_2$	3.5	0.93	0.59	0.16	0.05	1.2
Cycloolefins						
Cyclopentene	2.1	2.3	0.47	0.53	1.9[e]	0.10
Cyclohexene	41	48	3.5	4.0	1.0[d]	0.49
Cycloheptene	7.0	7.7	0.15	0.17	3.3[d]	0.03
Diolefins						
Butadiene-1,3	1.1	1.3	1.1	1.3	0.9	0.22
Butadiene-1,3-d_6	1.8	2.1	1.8	2.1	1.0	...
Acetylenes						
$CH_3C{\equiv}CH$	0.46	0.56	1.6	2.0	...	...
$CH_3C{\equiv}CD$	0.46	0.56	1.6	2.0	...	...
Aromatics						
Benzene	6.5	2.5	0.51	0.21	0.02[d]	0.82

[a] The values are relative to those of *cis*-butene-2 taken as unity. For comparison, the corresponding relative argentation constants at 0°, $(K_c/K_c^*)_{Ag^+}$, and the absolute values of the complexing constants, $(K_c')_{SF}$, for the pure silanized firebrick support in column V at 0° are also given. [b] The data are from ref 14, except where otherwise indicated. [c] Small negative values are obtained for pentene-1 and 3-methylbutene-1. [d] Extrapolated to 0° using the data measured at 40° in ref 12 and selecting appropriate temperature coefficients by analogy with related compounds in ref 14. [e] Extrapolated to 0° from the data at 25 and 40° in ref 14.

V). In this case, $(K_c')_{ol} \neq 0$ and eq 3 and 5 have to be altered to

$$K_a/K_a^* = [(t_r')_{ol} - \rho(t_r')_{par}]/[(t_r')_{ol} - \rho(t_r')_{par}]^* \qquad (6)$$

and

$$K_c/K_c^* = (t_n' - \rho)/(t_n' - \rho)^* \qquad (7)$$

where $\rho = t_n'$ for pure support (column V). The values of the relative equilibrium constants K_a/K_a^* and K_c/K_c^* calculated from eq 6 and 7 for the four iodine-coated columns show again reasonable mutual consistency, probably somewhat better than the corresponding values from eq 3 and 5 in Table III. A summary of the mean values for column I at the three flow rates used is given in Table IV. The two sets of data, from eq 3 and 5, on one hand, and from eq 6 and 7, on the other, show very similar trends with olefin structure. More pronounced differences are found for those unsaturated hydrocarbons which are more strongly retained on column V, such as trialkyl- and tetralkylethylenes and benzene. The $(K_c/K_c^*)_{I_2}$ and the $(K_c/K_c^*)_{Ag^+}$ values from the literature,[12,14] given in Table IV for comparison, show a remarkable similarity in the trends, especially so in the case of the $(K_c/K_c^*)_{I_2}$ data from eq 7. There are also some differences and these will be discussed later on in this article.

For the pure uncoated support (the silanized firebrick in column V) it can again be assumed formally that the greater retention of olefins than that of their structurally analogous paraffins is due to the specific interaction or "complexing" of the olefinic double bonds with the surface sites. It is possible in this case to evaluate the absolute rather than only the relative values of K_c' for the silanized firebrick (SF) since here

$$(K_c')_{SF} = \rho - 1 \qquad (8)$$

The values are listed in the last column of Table IV. Approximately, there is a continuous increase in $(K_c')_{SF}$ with the alkyl substitution of the olefins, suggesting an electrophilic ("acidic") character of the surface elements responsible for the greater retention of olefins and a lack of pronounced steric effects. The $(K_c')_{SF}$ represents the nondimensional equilibrium constant of complex formation as defined in this work, *i.e.*, it is *by definition* the dynamic ratio of the number of molecules complexed with the surface to those which are only physically adsorbed.

The Abnormal Broadening of the Chromatographic Peaks. The abnormally broad peaks (large H values) for some olefins, especially so for the terminal *n*-olefins, as partly shown in Table II, are symptomatic of non-

Table V. Secondary Deuterium Isotope Effects on the Iodine-Coated Silanized Firebrick, Column I, at 0°[a]

Olefin	$(K_c)_d/(K_c)_h$ I_2 (eq 9)	 Ag^+	Olefin	$(K_c)_d/(K_c)_h$ I_2 (eq 9)	 Ag^+
$CH_3CD{=}CH_2$	1.17	1.04	*cis*-$CD_3CD{=}CDCD_3$	1.24[b]	1.13
$CH_3CH{=}CD_2$	1.36	1.08	*trans*-$CD_3CD{=}CDCD_3$	1.04[b]	1.16
$CH_3CD{=}CD_2$	1.50	1.11	$CD_2{=}CDCD{=}CD_2$	1.46[b]	1.17
$CD_3CH{=}CH_2$	0.9	1.03	$CH_3C{\equiv}CD$	1.0	. . .
$CD_3CD{=}CD_2$	1.58	1.14			

[a] $(K_c)_d/(K_c)_h$ values are all given relative to the completely protiated isomer. The values for the corresponding Ag^+ complexes, taken from ref 14, are given for comparison. [b] Mean values at the three flow rates on column I, calculated from the data in Tables I and II.

equilibrium chromatographic effects.[15-18] They may be due to a lack of rapid equilibration of adsorption and desorption or to a slow formation and decomposition of iodine-olefin compounds. The two possibilities are formally similar. Yamazaki[19] has made use of Mellin transforms to derive an expression for excess peak broadening due to nonequilibration of adsorption and desorption on several adsorption sites. We have used his expressions to reproduce eq 3 and 5, as mentioned earlier, and to calculate from the excess peak broadening the values of a constant which, subject to some assumptions, should be equal to K_a/K_a^*. For lack of space, the derivations and the calculated values cannot be reported in the present paper and this aspect of the work, mainly only of chromatographic interest, will therefore not be further discussed at this time.

Secondary Deuterium Isotope Effects. The magnitude of the secondary deuterium isotope effect on the complexing of olefins with solid iodine is measured by the ratio $(K_c)_d/(K_c)_h$ (subscripts d and h refer to deuterated and nondeuterated species, respectively), which is given by the following expression (derived from eq 2)

$$\frac{(K_c)_d}{(K_c)_h} = \frac{(K_s)_h}{(K_s)_d}\frac{[(t_r')_{ol} - (t_r')_{par}]_d}{[(t_r')_{ol} - (t_r')_{par}]_h} \qquad (9)$$

The ratio $(K_s)_h/(K_s)_d$ can be expected to be slightly greater than unity because of the greater volatility of the deuterio isomers of hydrocarbons.[20] The values of $(K_c)_d/(K_c)_h$ calculated fom eq 9, assuming as a first approximation that $(K_s)_h/(K_s)_d = 1$, are listed in Table V. For comparison, the literature values[14] for the corresponding Ag^+ complexes are also given.

Before discussing the data in Table V, it has to be stressed again that the data for iodine are of very much lower accuracy than those for Ag^+. With the very broad peaks obtained with the propylenes, it is difficult to pinpoint the peak maxima with any accuracy. Nevertheless, the existence of relatively large secondary deuterium isotope effects is beyond doubt. The effects are considerably larger than are observed with Ag^+, but the over-all trends are remarkably similar. In this connection, the values for the various deuterated propylenes are of particular interest. It was found previously[14] that deuteration on the double bond (α effect) increased Ag^+ complex stability very much more than deuteration of the methyl group (β effect), and that the over-all effect was approximately logarithmically additive, as indicated, for example, by the empirical equation valid for Ag^+ complexes at 0°[21]

$$K_d/K_h = (1.040)^{n\alpha}(1.010)^{n\beta} \qquad (10)$$

The data for iodine are qualitatively very similar but have, unfortunately, a limited quantitative significance. The $(K_c)_d/(K_c)_h$ value of less than unity for $CD_3CH{=}CH_2$ is undoubtedly at least in part due to the simplifying assumption that $(K_s)_h/(K_s)_d = 1$. The retention time of propane on these columns is so short that it would be difficult to determine $(K_s)_h/(K_s)_d$ experimentally with adequate accuracy, and no attempt was made to do so. $(K_c)_d/(K_c)_h$ values for *cis*-C_4D_8-2 and 1,3-C_4D_6 are more or less in line with the magnitude of the α effect observed with the propylenes. The value for *trans*-C_4D_8-2, on the other hand, seems to be appreciably smaller than would be expected and seems to be definitely smaller than for the *cis* isomer, in contrast to the corresponding complexes with Ag^+.

On the pure silanized firebrick (column V) $(K_c)_d/(K_c)_h$ for *cis*-2-C_4D_8 and 1,3-C_4D_6 is very close to or perhaps slightly smaller than unity. The isotope effect is either absent, or it is very small and is largely compensated by a $(K_s)_h/(K_s)_d$ value somewhat larger than unity. The large isotope effects observed on the iodine-coated columns have therefore to be ascribed to the specific interactions of the olefins with the iodine deposit.

Discussion

Before discussing the trends in the values of the relative equilibrium constants summarized in Tables IV and V, it is worthwhile first to state briefly once again their physical meaning. K_a represents approximately the conventional equilibrium constant of adsorption of the gaseous olefin molecules on solid iodine (deposited on silanized firebrick). The present work provides only *ratios* of K_a values. There are no data in the literature with which to compare the K_a/K_a^* values in Table IV. The constant K_c in the present work has been devised as a measure of the excess interaction with solid iodine of the unsaturated hydrocarbons over that of their saturated structural analogs; as defined formally, K_c represents the equilibrium constant of complexing with solid iodine of the hydrocarbon molecules which are physically adsorbed on solid iodine. Again, only ratios of K_c values are provided and, once again, no data are available in the literature for direct comparison. The *ratios* of the equilibrium constants of complexing, as determined by conventional methods, may be expected to be similar although not necessarily identical

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(16) T. R. Phillips and D. R. Owens, "Gas Chromatography 1960," R. P. W. Scott, Ed., Butterworths, London, 1960, p 308.

(17) G. P. Cartoni, R. S. Lowrie, C. S. G. Phillips, and L. M. Venanzi, ref 16, p 273.

(18) J. J. van Deemeter, F. J. Zuiderweg, and A. Klinkenberg, *Chem. Eng. Sci.*, 5, 271 (1956).

(19) H. Yamazaki, private communication.

(20) W. E. Falconer and R. J. Cvetanović, *Anal. Chem.*, 34, 1064 (1962).

(21) In ref 14, eq. 10 is erroneously printed as $K_d/K_h = (1.040)^{n\alpha} + (1.010)^{n\beta}$.

with the K_c/K_c^* values in Table IV, since each system will have characteristics of its own. Unfortunately, even here, there are very few experimental data in the literature which can be used for a comparison. For the moment, it is more profitable to compare the present data for iodine with the corresponding literature data for Ag^+ complexes, as listed in Tables IV and V.

The principal trends in the (K_c/K_c^*) values for iodine may be summarized as follows.

(1) With increasing alkyl substitution of the olefinic double bonds, the values of the constants tend to decrease (rather than increase, as might be intuitively expected).

(2) *cis* isomers of internal olefins are more strongly complexed than the corresponding *trans* isomers.

(3) Deuterated olefins are generally more strongly complexed than their protio isomers, indicating an *inverse* secondary deuterium isotope effect.

(4) Deuterium atoms directly bound to the doubly bonded carbon atoms of olefins are particularly efficient in increasing complex stability, *i.e.*, the α-isotope effect is large while the β-isotope effect is small or zero.

(5) With the three cycloolefins studied, the complex stability is in the order cyclohexene > cyclopentene > cycloheptene.

The first four of these characteristics are closely analogous to the Ag^+–olefin systems.[14] The remarkable analogy between the K_c/K_c^* values in Table IV for iodine (especially of those obtained from eq 7) and for Ag^+ complexes with the open-chain olefins, in spite of the vastly different types of the systems used in the two studies, is one of the more interesting results of the present work. It suggests strongly that the main structural factors responsible for the stability of the complexes of alkenes with the Ag^+ ions in glycol solution and with solid iodine are closely related. Not surprisingly, there are also some quantitative differences such as, for example, the distinctly smaller relative values of $(K_c/K_c^*)_{I_2}$ for the 1,1-dialkylethylenes. While differences in the extent of steric interferences with the two acceptors, iodine and Ag^+, could be mentioned as a possible contributing factor responsible for differences of this kind, it is impossible to arrive at definitive conclusions at this time. The same holds true for the striking difference in the behavior of the three cycloolefins in the two systems; of the three, cyclohexene is the least strongly complexed with Ag^+ and it is the most strongly complexed with iodine. It is of interest that a similar reversal in the strengths of the cycloolefin complexes was found by Traynham and Olechowski[22] using the classical distribution and spectrophotometric techniques, although in their systems the order of stability was slightly different.

The $(K_c/K_c^*)_{I_2}$ value for benzene in Table IV is appreciably larger than the corresponding Ag^+ value. This result is probably genuine, although it has to be viewed in the light of the simplifying assumptions made in the present work and the accuracy of the data. The data plotted in Figure 1 show that the retentions of saturated hydrocarbons are mainly determined by the number of carbon atoms and are less sensitive to structural changes. For this reason the simplifying assumption implicit in eq 5 that the hypothetical retention of an olefin passing through the column without complexing with iodine is the same as that of a structurally analogous paraffin appears justified. For benzene, cyclohexane was taken as the saturated noncomplexing analog, and the validity of this procedure could perhaps be questioned in this case because of the appreciable structural and conformational differences. However, eq 7 does take account of the actually measured relative retention time of benzene and of the other unsaturated hydrocarbons on the uncoated support (column V) and is therefore not subject to the same objection. Nevertheless, it should be recognized that both the iodine and the Ag^+ value for benzene in Table IV are of lower accuracy because the effect due to complex formation represents only a relatively small fraction of the over-all effect of physical adsorption, in the former case, and of solution in the ethylene glycol solvent, in the latter.[12]

Ethylene forms a strong complex[12,14] with Ag^+, and the very small retention times for ethylene shown in Table II are somewhat surprising and may result from very small values for K_s. However, it is possible that the results with ethylene are an experimental artifact, with a small amount of ethylene being swept through the columns without undergoing complexing, as was observed even with propylene at higher flow rates of carrier gas. A more detailed study of the behavior of ethylene is necessary before it can be discussed in relation to the other olefins.

The secondary deuterium isotope effects found for the iodine–olefin complexes are larger than those shown by the corresponding Ag^+–olefin complexes. The similarity in the behavior of the variously deuterated propylenes in the two systems is very pronounced. The apparent lack of a β-isotope effect in the case of a complex of $CD_3CH{=}CH_2$ with iodine may be due to the fact that no correction was made for the opposing deuterium isotope effect on K_s. Potential interpretations of the secondary deuterium isotope effects found for electron donor–acceptor complexes have been discussed in considerable detail in an earlier publication[14] and are therefore not repeated here. In the present case the isotope effect for *trans*-2-butene appears to be distinctly smaller than for the *cis* isomer, even allowing for the low precision of the present data and in contrast to the corresponding complexes with Ag^+.[14] No explanation can be given except to suggest that with iodine variations in the magnitude of a "direct"[14] steric secondary deuterium isotope effect may perhaps be of greater importance than with the silver ions. Lack of an isotope effect in the case of $CH_3C{\equiv}CH$ and $CH_3C{\equiv}CD$, where the 1-hydrogen atom is coaxial with the carbon–carbon triple bond, could be interpreted to support such a view; however, in view of the complex nature of isotope effects of this kind,[14] it would be dangerous to draw conclusions on the basis of these observations alone.

It is of interest to compare the values for the constants $(K_c')_{SF}$ obtained with the pure silanized firebrick support with the K_c/K_c^* values for iodine and Ag^+. $(K_c')_{SF}$ shows a distinctly different trend: its value increases continuously with increasing alkyl substitution of the olefinic double bonds. A similar trend has been

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[22] J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

found previously for *sym*-trinitrobenzene (TNB)[15] and SO_2 complexes[23] with alkenes, and is the typical trend exhibited kinetically in some electrophilic reactions as, for example, when olefins are attacked by oxygen atoms.[24] Adherence to a simple electrophilic trend suggests that in these instances inductive effects of the alkyl substituents play the predominant role while steric interactions are of lesser importance. On the other hand, there are pronounced deviations from the expected electrophilic trend in Ag^+–olefin complexes and, as shown in the present work, similarly in solid iodine–olefin complexes. As discussed in greater detail before,[14] these deviations are most frequently ascribed to an important steric interference by bulky alkyl substituents and to changes in the magnitude of nonbonded repulsions in the olefin molecule because of the tendency of the trigonal carbon atoms to assume a partial tetrahedral configuration in the complex. The greater stability of the complexes of *cis* isomers is thus explained by the relief of strain due to the crowding of the two alkyl groups in *cis* position,[25] and an extension of this thought[26] ascribes the approximate correlation between the argentation constants and the heats of hydrogenation of some olefins to the similarity of effects of structural changes in the two processes. Although it is difficult to separate the various contributions to complex stability and to determine their relative importance in particular cases,[12,14] there is little doubt that configurational changes and direct and indirect steric effects must play an important role in the complexes of silver ion and solid iodine with olefins. In this connection it is of interest that no appreciable secondary deuterium isotope effects on the stability of the complexes have been found with TNB or silanized firebrick (K_{SF}'), but such effects are quite pronounced in the case of silver ion and iodine. It may thus appear that substantial configurational changes are a prerequisite for the existence of pronounced secondary deuterium isotope effects of this kind. However, further experimental information on related systems is necessary.

In concluding, a comment should be made in connection with the frequently expressed view that studies of iodine–olefin complexes may be difficult or impossible because of direct reactions of olefins with iodine. Such reactions have indeed been observed.[27,28] However, photolytic initiation seems to be essential.[28] In the present work, light could not penetrate into the columns and no difficulties of this nature were observed.

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The Reactions of Thermal Carbon Atoms in Rare Gas–Ethylene Matrices

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Abstract: The reactions of thermal carbon atoms with ethylene trapped in solid rare gas matrices have been studied. For comparison purposes, gaseous noble gas–ethylene mixtures were also examined. Free carbon atoms were produced as C^{11} by nuclear techniques and moderated to thermal kinetic energies by collision with the inert gas. As expected, Kr and Xe were found to be poorer moderators than Ne. However, in mixtures containing 99.5% Kr, virtually all carbon atoms react after thermalization, and, even in 99.5% Xe mixtures, hot reactions accounted for only a minor portion of the products observed. The results obtained provide few surprises; there is no departure from the trends predicted by the model for carbon atom reactions. Thermal carbon atoms form relatively low-energy adducts with ethylene, and these are rapidly collisionally deexcited in the solid phase. As a result, extensive fragmentation of the adduct is greatly diminished, and the yield of corresponding products, such as acetylene, is quite low. On the other hand, stabilization of the adduct to give allene becomes much more probable.

The chemistry of free carbon atoms in the ground (^3P) or low excited (^1D, ^1S) states[1] has been studied using C^{11} produced at high kinetic energies by nuclear processes, *e.g.*, $C^{12}(\gamma,n)C^{11}$. In a normal reagent system, such energetic atoms may undergo "hot" reactions. Only those which lose their excess energy in collisions in which they do not combine may subsequently undergo thermal reaction. By addition of an inert moderator, usually a noble gas, thermalization prior to reaction is favored and hot processes may be suppressed. The reactions of thermal carbon atoms with various gases have been studied in this way.[2-4]

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